Waterfalls as sources of small charged aerosol particles

L. Laakso, A. Hirsikko, T. Grönholm, M. Kulmala, A. Luts, T.-E. Parts

Atmos. Chem. Phys. Discuss., 6, 9297–9314, 2006
www.atmos-chem-phys-discuss.net/6/9297/2006/

Atmospheric Chemistry and Physics Discussions

Waterfalls as sources of small charged aerosol particles

L. Laakso[1], A. Hirsikko[1], T. Grönholm[1], M. Kulmala[1], A. Luts[2], and T.-E. Parts[2]

[1]Department of Physical Sciences, P.O. Box 64, 00014 University of Helsinki, Finland
[2]Institute of Environmental Physics, University of Tarto, Ülikooli 18, 50090, Tarto, Estonia

Received: 22 June 2006 – Accepted: 31 August 2006 – Published: 26 September 2006

Correspondence to: L. Laakso (lauri.laakso@iki.fi)

Abstract

In this study, we measured (to our knowledge, for the first time) the mobility distributions of cluster and intermediate ions with an ion spectrometer near a waterfall. We observed that the concentration of negative 1.5–10 nm ions was one-hundred fold compared to a reference point 100 m away from the waterfall. Also the concentration of positive intermediate ions was found to be higher by a factor of ten compared to the reference point. The increased concentration of negative intermediate ions is assumed to be due to the so-called waterfall effect. In the waterfall effect, autoionization causes free charges inside water droplets. These charges fluctuate and cause surface protrusions which produce free ions when a droplet collides with an obstacle. Differences between the polarities are supposed to be caused by the different interaction volumes of positive and negative ions and the formation of magical clusters in water. In addition to the waterfall effect, we assume that some of the ions of both polarities are formed in droplet breakup due to uneven distribution of charges inside the droplet.

1 Introduction

Aerosol particle formation in the atmosphere is a significant factor affecting both climate and the ecosystem. In addition to large-scale particle formation (Kulmala et al., 2004), new particles are also observed to form in a limited spatial scale. One special case of nucleation mode particle appearance is the breakup of small water droplets (Hõrrak et al., 2005, 2006). These observations shows the formation of new, especially negatively charged intermediate ions related to rain.

Recent investigations suggest that intermediate air ion formation may also take place near waterfalls (Luts et al., 2004). The effect of waterfalls on the electrical status of the adjacent environment has been known for more than a century. As early as the early 1890s Lenard (1892) showed that the air becomes negatively charged near waterfalls. He also demonstrated that the effect only arises when moving liquid is sprayed at an

obstacle. A simple water jet, for example, was not found to generate such an effect.

Recently, several authors have discussed charge formation (e.g., ion evaporation, Coulomb explosion, charge residue) in liquid droplets (Iribarne and Thomson, 1976; Znamenskiy et al., 2003; Vostrikov et al., 2006). Their experiments showed that in some cases small ions are able to separate from evaporating charged droplets.

However, despite prior knowledge, there are no number size distribution measurements of ions carried out in the vicinity of a waterfall. The case of waterfalls differs from, for example, rain, since bulk water is originally electrically neutral whereas rain droplets may be originally charged due to their formation processes in the clouds. Thus, in case of a waterfall, the key questions are how do we get neutral water droplet split into charged particles and what are the sizes and charges of the resulting particles.

In this study, we first introduce two potential ways to obtain charged particles from a waterfall. Then we describe the instruments used in this study together with the experimental setup and then present the first ion size distribution observations from the area adjacent to a waterfall together with reference measurements. Finally, we utilize several theoretical approaches to explain the measured results.

2 Theoretical background

The phenomenon of how waterfalls produce ion is far from being completely understood. Here we propose two different paths which can produce nanometer sized water particles (Fig. 1).

2.1 Path I: Surface protrusions as a source of negative intermediate ions

According to Coehn (1928), the outer shell of a water droplet becomes negatively charged, even in the case where free charges do not exist and the whole droplet is electrically neutral. If the droplet collides with a surface, a small outer fragment can become disjointed. Then a small fragment with negative charge(s) goes into the air,

whereas the remaining positive charge stays in the larger droplet. In the presence of chemical impurities (e.g., sodium chloride), the solution ions change the shape of the droplet shells. In this case a collision can lead to a positively charged water fragment. Coehn mainly provides a qualitative analysis, but within the qualitative limits he can explain the known observation results. Below we explain each of four different steps needed for ion (charged water particle) formation.

I-1 Origin of free charges in a droplet

Where are the charges inside the original droplet from? A certain number of the free ions in bulk water is generated by the autoionization of water molecules, which results in H_3O^+ and OH_ ions:

$$H_2O + H_2O \xrightarrow{k_w} H_3O^+ + OH^- \quad (1)$$

where $K_w=[H_3O^+][OH^-]/[H_2O]\approx 10^{-14}$. Where pH=7, $[H_3O^+]=[OH^-]\approx 10^{-14}$. The water autoionization equilibrium constant K_w at 25°C equals 1.01×10^{-14}, and at 0°C the constant K_w is 1.14×10^{-15} (e.g. Brown et al., 2006). Thus, at temperatures below 25°C, the concentration of free ions does not exceed 0.1 ppm (one H_3O^+ and OH^- ion pair per ten million water molecules). To obtain free charges due to autoionization, the droplet should contain at least 10^7–10^8 water molecules.

Inside a droplet the charge rearrangement is to some extent random. However, a random rearrangement does not provide a configuration where the negative charges are concentrated near the drop surface, which is needed for the production of small charged fragments. To override the randomness of the process, and get charged surface fragments, we need to multiply the required 10^7–10^8 water molecules, say, at least, by hundred. The resulting droplet, consisting of at least 10^{10} molecules has a diameter of about one micrometer. Thus, structured water molecule orientation is possible only in super micrometer droplets.

I-2 Break-up of droplets

Next enough kinetic energy is needed to break the droplets and to separate the ions from the droplets. For drops consisting of 27 water molecules without free charges, charges only emerge at drop velocities of about 10 km/s (Znamenskiy et al., 2006). What about the larger droplets? The kinetic energy should provide the energy necessary to form the surfaces of both droplets.

First, we have assumed that a droplet of a certain size collides with a surface and produces two new droplets. When one droplet is split into two parts, the sum of the surface energies of these new droplets is larger than the surface energy (E_s) of the original droplet ($E_s=\sigma\times A_1$, where σ is the surface tension and A_1 area of the original droplet). In the case of a waterfall, this energy increase can be due to the kinetic energy (E_k) of the falling water droplets ($E_k=\frac{1}{2}m_1 v(d_1)^2$, where m_1 is the mass of original droplet and $v(d_1)$ its velocity). We have calculated several droplet combinations and velocities (kinetic energies of original droplets) needed for new droplet formation (see Table 1). From the table, we can see that 1) a droplet with a diameter down to about a micrometer breaks up relatively easily; 2) it is easier to detach a small fragment than a larger fragment. In the case of larger droplets the required energy corresponds to the velocities found in waterfalls.

I-3 Protrusions

Due to fluctuations, the charges can concentrate within small volumes of the liquid (Iribarne and Thomson, 1976). According to Znamenskiy et al. (2003), the surface of the droplet bears both shape deformations and fluctuations, whereas the magnitude of these fluctuations depends on the charge concentration within the region. These surface protrusions serve as the intermediate stage preceding ion ejection. Finally, the droplet regions with enhanced concentrations of (rearranged) ions can detach easier.

I-4 Differences in the properties of negative and positive fragments

According to Lenard (1892), negative charges tends to appear in the air and positive charges tends to stay in the liquid. Why is this? One explanation is that protons always tend to attract large numbers of water molecules around them. The proton mobility in water is much larger than the mobility of a OH^- ion. Therefore, a proton interacts in a much larger water volume than a OH^- ion. Also the proton induces a number of stable proton clusters, sometimes called magical ones. $H_3O^+(H_2O)_{20}$ is one of these "magical" ion clusters (Hulthe et al., 1997). The neutral water clusters also tend to contain certain "magical" numbers of molecules, e.g. $(H_2O)_{21}$. Also, $(H_2O)_{280}$ has been proposed (Iribarne and Thomson, 1976; Chaplin, 2000, 2006) .

In addition to different interaction volumes, H_3O^+ tends to be surrounded of many neutral water molecules, whereas OH^- tends to be more free. For example, the following reaction is likely to take place:

$$H_2O + (H_2O)_{21} \rightarrow H_3O^+(H_2O)_{20} + OH^- \quad (2)$$

As a result of the above reaction, a small OH^- ion is released and the larger $H_3O^+(H_2O)_{20}$ stays in the water. This is one of the similar reactions which can explain the sign dependence in favor of negative intermediate ions.

2.2 Path II: Evaporation of droplets formed in collisions

Waterfalls produce a large number of droplets due to mechanical energy. Because of autoionization and statistical fluctuations of charges inside a droplet, some of the droplets formed via collisions may carry more positive, some more negative charges. When droplets are transported away from a waterfall, relative humidity decreases and the droplets start to evaporate. This process produces approximately equal number of negative and positive ions. The size distribution of these ions is continuous covering a wide range of sizes.

3 Instruments

We measured waterfall-produced ions with two Air Ion Spectrometers (AIS) (Laakso et al., 2004; Airel Ltd.). AIS measures the mobility distributions of air ions: naturally charged clusters and aerosol particles. The spectrometer consists of two identical cylindrical aspiration-type differential mobility analyzers, one for measuring positive ions and the other for negative ions. Each mobility analyzer has 21 collector electrodes provided with individual electrometrical amplifiers for measuring the electrical current carried by ions of different mobilities. The air sample containing ions is sucked into the mobility analyzer through the electronically controlled electrostatic filter (switched on/off). The filter removes (switched on) the ions from the sample when the offset levels of the measuring electronics are measured for data quality monitoring purpose. Otherwise the filter is switched off. The time resolution of the AIS is typically five minutes, the time used in our experiments, during that time sample and offset level mobility distributions are measured in turn.

The estimations of diffusion broadening and losses of ions and data inversion are based on a theoretical treatment by Airel Ltd. (Fuchs, 1964; Tammet, 1970). Recently the AISes and their inversion procedure have been calibrated in the laboratory down to 2 nm and below that by comparing the devices to the other type of ion spectrometer, Balanced Scanning Mobility Analyzer (BSMA, Airel Ltd.), which is considered to be an etalon device (Tammet, 2004, 2006).

In our experiments the mobility range of AISes was 0.00133–3.16 $cm^2V^{-1}s^{-1}$. The mobility distributions of ions are presented by 28 logarithmically uniformly distributed fractions. According to Tammet's algorithm (1995) the diameter range is 0.34–40 nm in normal temperature and pressure (273 K and 1 atm), which are assumed here when converting the mobilities to diameters. We have to note that conversion from mobility to diameter assumes only one charge per cluster/particle. In the atmosphere this assumption is good enough for small particles due to their low charging probability (e.g. Fuchs, 1964). However, in the case of waterfalls, artifacts in size can arise if droplets

are multiple charged depending on their formation processes.

In addition to air ion spectrometers, we used a Delta OHM DO 9847 logger with Pt100 and Mk-33 sensors to measure temperature, relative humidity and pressure. The total aerosol particle number concentration was measured with two TSI Model 3007 condensation particle counters with a cut-off size of 10 nm. The two CPC's were compared side by side with ambient particle concentrations 2000–40 000 cm^{-3} and the results were corrected by the offset factor (equal to 0.9) obtained from the comparison, using the lower concentration as a reference.

4 Measurements

The measurements were carried out at Vantaanputous (Fig. 2), a waterfall ca. 5 km North-East from downtown Helsinki. The waterfall is located near a road which is around 100 m away from the measurement point. The River Vantaa is a typical Southern Finland river with a relatively high clay content. On the 15 November 2005 the total suspended mass (measured with 0.4 μm membrane filters 1.4 km upriver from our measurement point) was 100 mg/l (K. Lahti, personal communication, and Vahtera et al., 2005). The height of the fall is approximately 10 m which produces a maximum velocity of 14 ms^{-1} assuming free gravitational fall.

We carried out our measurements during two days, 11 November and 18 November 2005. Both days were relative cold and the humidity was high (Table 2). On 11 November we measured for one and half hours and on 18 November for over four hours.

Two air ion spectrometers were utilized: one on the bridge approximately 20 m from the edge of the waterfall and a reference measurement 100 m from the waterfall to the side of the mean wind. Wind direction was measured with a humid finger method and this empirical data, together with visual estimation of the traffic density on different roads was used while choosing the reference point. Due to technical problems (a locked gateway) during the second measurement day, the AIS on the bridge was located on the eastern end of the bridge.

Before starting the measurements, we compared the two AISes by running them side-by-side for an hour in order to detect the possible offset between the devices. When interpreting the charged particle concentrations and size distributions the data of AIS at the waterfall was multiplied by the size dependent coefficients obtained from comparison measurements. The average correction factor for positive ions was 1.02 and for negative ions 1.23. We assumed that differences between the AISes were the same during the experiments.

5 Results and discussions

Figure 3 shows the size distributions of negative and positive ions. During both days, there was a clear difference between the waterfall and the reference in the concentration of 1.5–10 nm ions. The difference was more pronounced for negative ions, but also the concentration of positive ions was enhanced. When we compare concentrations of negative and positive ions at the reference point from both days, we notice that the concentrations were relative equal, as they should be without sign-dependent intermediate ions sources nearby.

Figure 4 presents the ratios of ion concentrations at the waterfall to those at the reference point. The concentration of negative ions in the size range of 1.5–10 nm was up to 120 fold at the waterfall. There was also approximately a ten-fold increase in the concentration of positive ions.

Another interesting feature is the difference in the widths of the distributions between the two days which may be due to the differences in the autoionization rates at different temperatures. However, with only two days of data, reasons for this difference remain speculative. There was also a difference in the size of the maximum concentration. The maximum of negative ions is made of up of slightly smaller sizes (2 nm versus 2.5 nm for positive) which supports the protrusion theory presented earlier in this paper.

Table 2 summarizes the median characteristics of our measurements. The upper size limit for the cluster ions is approximately 1.5 nm. We used that value as a lower

limit when calculating differences in the intermediate ion concentrations between the waterfall and the reference point. From the table we notice that there was a clear difference between the two days that we performed measurements: during the first observation day the difference is several times higher than during the second day. This is in contrast with the water flow rates in the river Vantaa. We attribute this difference mainly to the differences in wind directions, since measurements of a single point (line) source like a waterfall are sensitive to even small changes in wind directions. Additionally, there may have been a small difference in autoionization rates due to the lower temperature during the second measurement day. However, the general conclusions for both days are qualitatively similar.

As explained in Sect. 3, we tried to avoid experimental errors by comparing the devices side-by-side and calibrating them carefully in the laboratory. However, there are also natural sources of errors which can lead to misinterpretation of results. One of our main concerns was the possible background contamination of the nearby road. We studied this effect with two portable CPC's and found that the concentrations and their time behavior were relative equal in both places, waterfall and the reference point (Table 2). However, concentrations at the bridge were slightly higher, probably due to larger (>10 nm) ions produced by the waterfall.

6 Conclusions

In this study, we present for the first time ion size distribution observations in the vicinity of a waterfall. We found that waterfalls produce intermediate, mainly negative ions. The concentration of the negative ions between 1.5 and 10 nm at the waterfall was more than 100 times higher than at reference point. Also, the concentration of positive ions was increased by a factor of ten. The maximum concentration of waterfall produced negative ions was at 2 nm whereas the maximum of positive ions was at 2.5 nm.

Formation of negative ions is assumed to be caused by fragmentation of water droplets assisted by protrusions. In addition, positive and negative ions are produced

by evaporation of charged water droplets formed in collisions. Differences in the maximum sizes between positive and negative ions are assumed to be due to formation of magical water clusters in water droplets.

Acknowledgements. The authors want to thank the following people for their help: J. Ylönen from the Finnish Museum of Technology for his help and especially providing us with electricity; M. Huttunen/the Finnish Environment Institute and K. Lahti/Vantaanjoen ja Helsingin seudun vesiensuojeluyhdistys for data related to the river Vantaa; M. Dal Maso and M. Vana for their help with transportation. A. Hienola is acknowledged for test-reading the manuscript. In addition, the Estonian Science Foundation (grants no. 6223 and 5387) and the Maj and Tor Nessling Foundation (grant no. 123) are acknowledged for funding.

References

Airel Ltd., E.: http://www.airel.ee. 9303

Brown, T., LeMay, H. E., and Bursten, B. E.: Chemistry – The Central Science, Pearson Education, Inc., 2006. 9300

Chaplin, M.: Water Structure and Behavior, http://www.lsbu.ac.uk/water/, 2006. 9302

Chaplin, M. F.: A proposal for the structuring of water, Biophys. Chem., 83, 221–221, 2000. 9302

Coehn, A.: Elektrizitätsbewegung in Festen und flüssigen Körpern, chap. Wasserfallelektrizit, pp. 350–358, Springer-Verlag, Berlin, 1928. 9299

Fuchs, N. A.: The mechanics of Aerosol, Pergamon, New York, 1964. 9303

Hõrrak, U., Tammet, H., Aalto, P., Vana, M., Hirsikko, A., Laakso, L., and Kulmala, M.: Formation of charged nanometer aerosol particles associated with rainfall, in: Proceedings of European Aerosol Conference 2005, Ghent, Belgium, edited by: Maenhaut, W., p. 606, 2005. 9298

Hõrrak, U., Tammet, H., Aalto, P., Vana, M., Hirsikko, A., Laakso, L., and Kulmala, M.: Formation of charged nanometer aerosol particles associeted with rainfall: atmospheric measurements and lab experiments, in: Proceedings of BACCI, NECC and FCoE activities 2005, edited by: Kulmala, M., Lindroth, A., and Ruuskanen, T., vol. 81B of "Report Series in Aerosol Science", pp. 180–185, 2006. 9298

Hulthe, G., Stenhagen, G., Wennerström, O., and Ottosson, C.-H.: Water clusters studied by electrospray mass spectrometry, J. Chromatogr. A., 777, 155–165, 1997. 9302

Iribarne, J. and Thomson, B.: On the evaporation of small ions from charged droplets, J. Chem. Phys., 64, 2287–2294, 1976. 9299, 9301, 9302
Kulmala, M., Vehkamäki, H., Petäjä, T., Dal Maso, M., Lauri, A., Kerminen, V.-M., Birmili, W., and McMurry, P.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004. 9298
Laakso, L., Anttila, T., Lehtinen, K., Aalto, P., Kulmala, M., Hõrrak, U., Paatero, J., Hanke, M., and Arnold, F.: Kinetic nucleation and ions in boreal particle formation events, Atmos. Chem. Phys., 4, 2353–2366, 2004. 9303
Lenard, P.: Über die Elektrizität der Wasserfälle, Ann. Phys., 46, 584–636, 1892. 9298, 9302
Luts, A., Noppel, M., and Vehkamäki, H.: Effect of sulfuric acid on the composition of negative small air ions: a numerical simulation, in: J. Aerosol Sci., EAC 2004 abstract book, 2004. 9298
Tammet, H.: The aspiration method for the determination of atmospheric ion-spectra, IPST for NSF, p. 208, 1970. 9303
Tammet, H.: Size and mobility of nanometer particles, clusters and ions, J. Aerosol Sci., 26, 459–475, 1995.
Tammet, H.: Balanced Scanning Mobility Analyser, BSMA, in: Nucleation and Atmospheric Aerosols 2004: 16th International Conference, edited by: Kasahara, M. and Kulmala, M., 294–297, 2004. 9303
Tammet, H.: Continuous scanning of the mobility and size distribution of charged clusters and particles in atmospheric air and the Balanced Scanning Mobility Analyzer BSMA, Atmos. Res., accepted, 2006. 9303
Vahtera, H., Muukkonen, P., Männynsalo, J., and Lahti, K.: Vantaanjoen yhteistarkkailu: Vedenlaatu vuosina 2000–2004, 56, Vantaanjoen ja Helsingin seudun vesiensuojeluyhdistys ry, 2005. 9304
Vostrikov, A. A., Drozdov, S. V., Rudnev, V. S., and Kurkina, L. I.: Molecular dynamics study of neutral and charged water clusters, Computational materials science, 35, 254–260, 2006. 9299
Znamenskiy, V., Marginean, I., and Vertes, A.: Solvated ion evaporation from charged water nanodroplets, J. Phys. Chem., 107, 7406–7412, 2003. 9299, 9301
Znamenskiy, V., Marginean, I., and Vertes, A.: Molecular dynamics study of neutral and charged water clusters, Computational Materials Science, 35, 254–260, 2006. 9301

Table 1. Velocity needed to break up a water droplet of a certain size. d_1: diameter of original water droplet; $N(d_1)$: number of water molecules in the original droplet; d_2: diameter of the smaller droplet formed in collision; $v(d_1)$ velocity needed for breaking the falling droplet (of diameter d_1).

Initial droplet		One of the resulting droplets	Velocity needed to produce droplet d_2	One of the resulting droplets	Velocity needed to produce droplet d_2
d1 [mm]	$N(d_1);H_2O$	d_2 [mm]	$v(d_1)$ [m/s]	d_2 [mm]	$V(d_1)$ [m/s]
2	1.4e21	1	0.3	0.2	0.1
1	1.8e20	0.5	0.4	0.1	0.1
0.4	1.1e19	0.2	0.6	0.04	0.1
0.2	1.4e18	0.1	0.8	0.02	0.2
4.0e-02	1.1e16	2.0e-02	1.9	4.0e-03	0.5
2.0e-02	1.4e15	1.0e-02	2.7	2.0e-03	0.6
4.0e-03	1.1e13	2.0e-03	6.0	4.0e-04	1.4
2.0e-03	1.4e12	1.0e-03	8.5	2.0e-04	2.0
4.0e-04	1.1e10	2.0e-04	19.0	4.0e-05	4.5
2.0e-04	1.4e09	1.0e-04	26.9	2.0e-05	6.4
4.0e-05	1.1e07	2.0e-05	60.1	4.0e-06	14.3
2.0-05	1.4e06	1.0e-05	85.0	2.0e-06	20.2
8.0e-06	9.0e04	4.0e-06	134.3	1.0e-06	39.6
4.0e-06	1.1e04	2.0e-06	190.0	1.0e-06	106.8

Table 2. Basic characteristics of the two observation days.

	11 November 2005	18 November 2005
Median T [°C]	9.8	0.8
Median *RH* [%]	76.5	71.0
Water flow $m^3\ s^{-1}$	10.9	22.8
N_{tot} (ref) [cm^{-3}]	19 978	24 649
N_{tot} (water fall) [cm^{-3}]	14 909	27 412
Difference (waterfall - reference)		
Negative ions 1.5–10 nm [cm^{-3}]	5410	1565
Positive ions 1.5–10 nm [cm^{-3}]	562	220

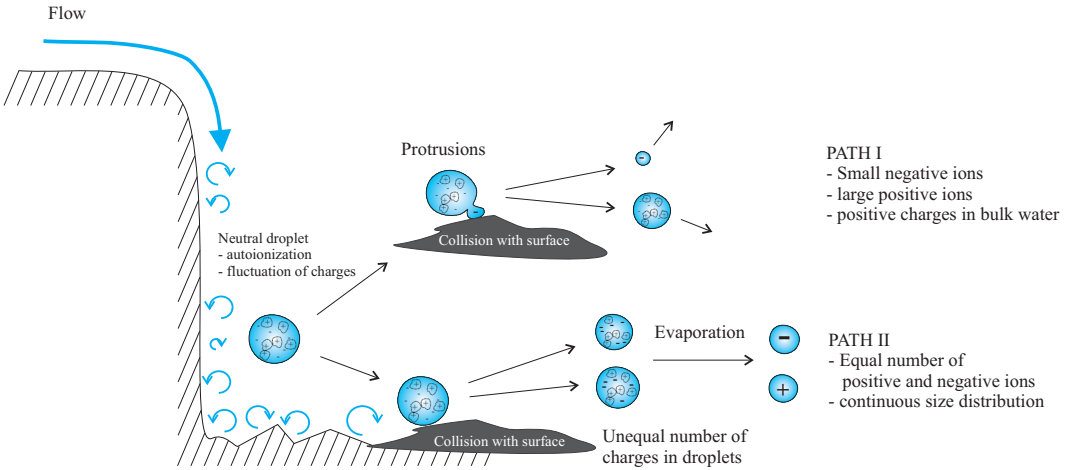

Fig. 1. Production of small charged particles in the vicinity of a waterfall. Paths I and II are discussed in more detail in the text.

Fig. 2. The Vanhankaupunginlahti barrage with two happy measurers. AIS measured on the bridge. The reference measurement place was about 100 m right (East) from the bridge. The closest road is located behind the building in the middle of the picture.

ACPD
6, 9297–9314, 2006

EGU

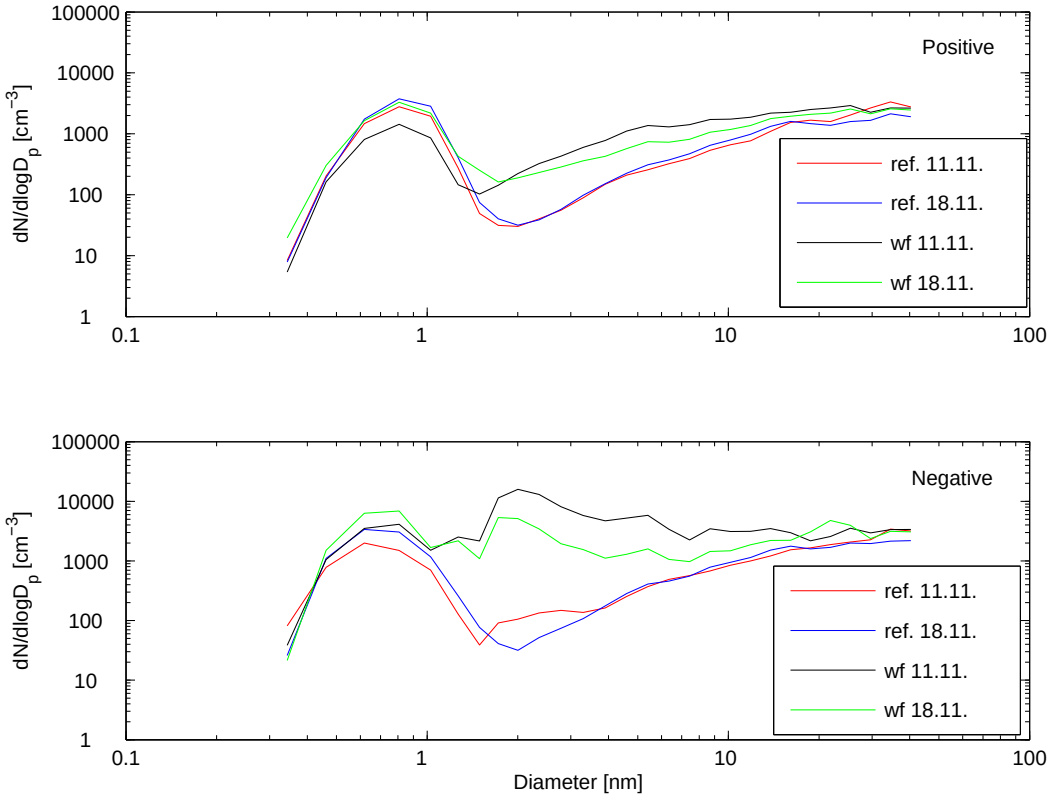

Fig. 3. The median size distributions of positive and negative ions at the waterfall (wf) and at the reference point (ref) (11 November and 18 November 2005).

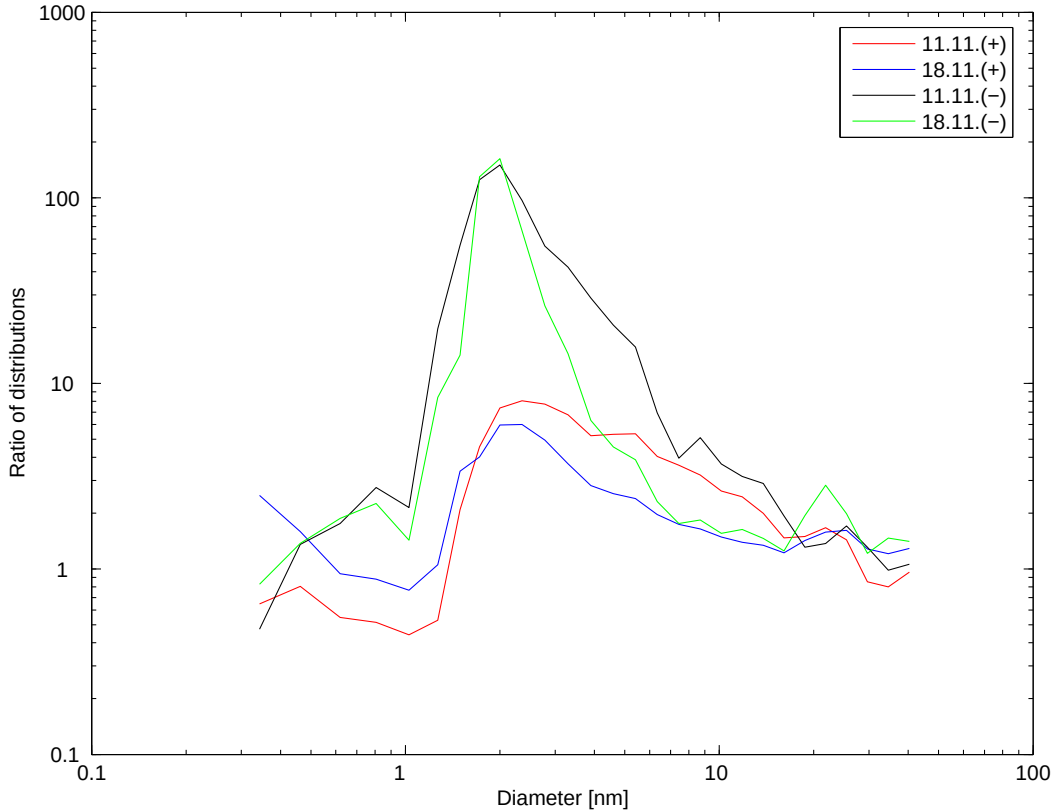

Fig. 4. The ratios of positive and negative ion concentrations at the waterfall to the concentrations at the reference point.

ACPD
6, 9297–9314, 2006